[Regular Paper]

High Strength Polyacrylamide/nmSiO₂ Composite Hydrogel for Well Killing

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Killing pills of high strength composite hydrogel were prepared by polyacrylamide, chromium acetate cross-linker and silica nanoparticles reinforcer. The killing performance of composite hydrogel depended on its viscoelasticity and compression strength, which were both influenced by polymer content, ratio of polymer to chromium acetate and nano silica content. In this work, the effect of these altering factors on strength of composite hydrogel were evaluated, results showed that elastic moduli (G'), viscous moduli (G'') and compression strength all increased as polymer content increased, ascribing to close entanglement among polymer chains and increasing crosslinking density. G' was proportional to the ratio of polymer to chromium acetate, whereas G'' and compression strength experienced initial increase then decrease, indicating an optimal ratio existed to achieve the strength peak of composite hydrogel. Silica nanoparticles contributed significantly to viscoelasticity and compression strength of hydrogel. From SEM images, we can see silica nanoparticles attached onto network branches and filled into the network pores in aggregation, in this dispersion form to strengthen the microstructure further to enhance the strength of composite hydrogel. Moreover, the polymer/nmSiO₂ composite system is shear-thinning fluid, which promises its pumpability as killing fluid during killing operation.

Keywords

Composite hydrogel, Silica, Viscoelasticity, Compression strength, Well killing

1. Introduction

In the process of drilling, open hole completion and/or workover in underbalanced condition, hydrostatic pressure in wellbore could be lower than formation pressure, and pressure difference produced always led to reservoir oil and gas underground flowing into the wellbore, resulting in a potential risk of well blowout. To avoid the potential risk, completion and tripping have to be conducted under the aid of snubbing operation device or Downhole-Deployment Valve (DDV)¹⁾. However, the rubber core of rotating blowout preventer affiliating snubbing operation device did not seal screen pipe at the wellhead. Meanwhile, besides high cost of large complicated equipment²⁾, DDV was easily damaged since hole deviation occurred in drilling³⁾. Additionally, regular killing fluids used for well killing had certain reservoir damage of lost circulation and formation pollution^{4),5)}. Facing these challenges, solid free killing fluids and clean spacing fluids^{6),7)} that separated regular killing fluids from reservoir were ever used for well killing to reduce damage to reservoir. Among these, L. Nwoke *et al.*⁸⁾ used water-soluble

polymers and crosslinker preparing hydrogel for killing well application, but low strength of the hydrogel cannot withstand formation pressure solely, as a result, heavier fluid had to be injected on top of the hydrogel to increase wellbore hydrostatic pressure. R. Arangath *et al.*⁹⁾ combined whole underbalanced drilling technology with solid-free viscoelastic fluids to realize drilling and completion of low permeability reservoir, however, clean spacing fluids were still needed additionally to prevent reservoir damage. Although polymer hydrogel for well killing application was studying popularly around the world¹⁰⁾, its disadvantages, such as low strength and toughness, failure to make itself endure high formation pressure, neither prevent harmful gas escaping from formation, especially the formation pressure coefficient goes above 1.0^{11)~13)}. Herein we added silica nanoparticles¹⁴⁾ into polymer crosslinking system to enhance the strength of hydrogel. The advantages of rigidity and thermal stability of inorganic silica were incorporated, combining with elasticity and ductility of polymer to prepare high compression strength nanocomposite hydrogel successfully for well killing application, which is both cost-efficient and killing-effective, besides a specific length of composite hydrogel column hanged on wellbore achieved to balance formation pressure solely, finally replacing snubbing operation device and Downhole-Deployment

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Valve (DDV) for well killing. In this paper, high strength nanocomposite hydrogel was prepared for well killing, and altering factors that effected viscoelasticity and compression strength of hydrogel were all discussed, especially the strength of silica nanoparticles, moreover the enhanced mechanism of silica particles on hydrogel strength was also explored.

2. Experimental

2.1. Materials

Partially hydrolyzed polyacrylamide (HPAM) with number average molecular weight of 8×10^6 - 10^7 and hydrolysis degree of 15 % was obtained from SNF (China) flocculant company in the form of white powder. Chromium acetate was obtained from Shanghai branch of Shanxi Xiaxian Yunli Chemical Co., P. R. China in the form of dark green solution. Silica nanoparticles, with particle size of 50-60 nm, was obtained from Zhejiang Yuda Chemical Co., P. R. China in the form of white powder.

2.2. Preparation of Polymer Nanocomposite Hydrogel

Silica nanoparticles were added into deionized water under stirring, with ultrasonic oscillation for 15 min, followed by continuous stirring for 1 h to obtain suspension solution, then polyacrylamide powder was added to the suspension solution with continuous stirring for 4 h to obtain homogeneous polymer solution. Later chromium acetate solution was added dropwise into polymer solution with additional 30 min stirring to obtain composite crosslinking solution. The final composite crosslinking solution was placed under the temperature of 70 °C for additional gelation time of 9 h, then the nanocomposite hydrogels were obtained.

2.3. Rheological Property

Viscoelasticity and thixotropic properties of hydrogels were measured using HAAKE RS600 version rheometer (HAAKE Co., German). For viscoelasticity, the measuring sensor was plate-to-plate geometry with a gap of 3 mm. The samples were cut into uniform dimension with diameter of 2 cm and height of 3 mm. The measurements were firstly set in an oscillation scan model with a stress range of 0-250 Pa and frequency of 0.5 Hz to obtain a linear viscoelastic extent, in which subsequent frequency-sweep tests were performed at a fixed stress of 50 Pa and frequency of 0.4 Hz or 0.5 Hz to obtain elastic modulus (G') and viscous modulus (G'') curves as a function of time. For thixotropic property, 20 mL of sample was poured into testing cylinder sensor of Z41 Ti model with a shearing rate of 0.001-1000 s^{-1} to ascertain the type of fluid. The tests were all carried out at 30 °C.

2.4. Compression Strength Measurements

Compression strength were measured using self-designed compression strength tests device¹⁵⁾, as shown

(1) Nitrogen cylinder; (2) Pressure reducing valve; (3) Buffer tank; (4) Six-port valve; (5) Pressure gauge; (6) Liquid storage tank (stainless steel casing); (7) Temperature controller; (8) Pressure sensor; (9) Computer.

Fig. 1 The Device of Compression Strength Test

in Fig. 1, which simulated killing well field application where nanocomposite hydrogel was injected into well-bore as killing fluids to resist the formation pressure. The fresh composite crosslinking solution was firstly poured into a stainless steel casing with a diameter of 42 mm and height of 336 mm. With both ends sealed, the casing loaded crosslinking solution was placed under temperature of 70 °C for overnight. After cross-linking system gelatinized, one end of the steel casing was opened to atmosphere, whereas the other was connected to the bottom of testing device through pipeline. The nitrogen flowed at a rate of 0.5 mL/min to the bottom of casing tube to impose increasing pressure on composite hydrogel. After the nitrogen pressure went up to a critical value beyond which the hydrogel was broken through, failure to standing nitrogen pressure again, this critical point was defined as compression strength of the hydrogel. The testing temperature was maintained at 70 °C by temperature-measured and -controlled apparatus.

2.5. Environment Scanning Electron Microscope

Microstructure of hydrogel and distribution of silica nanoparticles were observed by quanta 200F environmental scanning electronic microscopic (ESEM) (FEI Co., USA), with annular gaseous secondary electron detector (GSED) chosen. Fresh gel sample of 0.10 mL was frozen to -45 °C with liquid nitrogen, then observation was carried on with the sample slowly sublimating.

(a) Stand upright, (b) upside down.

Fig. 2 The Static Strength of Composite Hydrogel

3. Results and Discussion

3.1. Behavior of Composite Hydrogel with Increasing Polymer Content

With the ratio of polymer to chromium acetate crosslinker of 10 : 1, silica content of 1 %, the static strength of composite hydrogels was studied according to polymer content ranging from 1 to 3 %. The effect on static strength of composite hydrogel was present in **Fig. 2**.

When the beaker containing hydrogels stood upright, the static strength of composite hydrogels with polymer content varying from 1 to 3 % almost present no difference. Whereas inverted, the hydrogel at low polymer content of 1 % showed high fluidity of viscoelastic fluid, without adhering to the wall of beaker because of low viscosity, resulting in its flowing out of the beaker. At medium polymer content of 2 %, the hydrogel adhered to the bottom of beaker, with partial fluidity, and hung along the wall of beaker after inverted, indicating the strength became larger than that with polymer content of 1 %. The behaviors of hydrogel showed between viscoelastic fluid and solid. At high polymer content of 3 %, the hydrogel showed little fluidity, with hydrogel bulk adhering to the bottom of beaker, no hollow or hanging appeared on the surface of hydrogel, suggesting the strength of hydrogel was close to viscoelastic solid. The static strength of hydrogel increased significantly with increasing polymer content. The reason can be explained that more polymer chains entangled among each other, and the amount of carboxyl group that crosslinked with chromium acetate was increased owing to the increasing polymer content simultaneously, which increased the crosslinking density and enhanced the hydrogel strength.

Fig. 3 Elastic Moduli (G') and Viscous Moduli (G'') of Composite Hydrogel with Varying Polymer Content

Figure 3 present the effect of polymer content on elastic moduli (G') and viscous moduli (G''), the curves of which varied as the function of time at a constant stress of 50 Pa and frequency of 0.5 Hz. As shown in **Fig. 3**, elastic moduli (G') and viscous moduli (G'') of composite hydrogel with polymer content of 1 % was 6-10 Pa and 4 Pa, respectively, G' and G'' with polymer content of 2 % was around 40 Pa and 9 Pa, while G' and G'' with polymer content of 3 % was almost 100 Pa and 18 Pa, indicating that both G' and G'' increased obviously with increasing polymer content, and G' remained larger than G'' with $\tan \delta$ (G''/G') < 1, suggesting that composite hydrogel was viscoelastic solid dominated by elastic moduli¹⁶⁾. As polymer content increased, the composite hydrogel had high crosslinking density. When subjected to shear, dense network structure of composite hydrogel was involved to resist the applied stress, resulting in large amount of excess energy dissipated successfully. Besides, owing to the increase of crosslinking density, the same amount of free water was trapped by more crosslink chains, which restrained the flowing of free water and stored more energy by elastic deformation. Elastic (G') and viscous moduli (G'') showed the ability to store and dissipate energy, that is why both G' and G'' increased with increasing polymer content.

3.2. Performance of Composite Hydrogel with Varying Ratio of Polymer to Crosslinker

A range of nanocomposite hydrogels were studied the effect of ratio of polymer to crosslinker on its viscoelasticity. In view of varying polymer-crosslinker ratio, polyacrylamide and silica content was kept stable at 2 % and 5 %, respectively. As shown in **Fig. 4**, elastic moduli (G') increased sharply as the ratio decreased (crosslinker content increased), whereas viscous moduli (G'') nearly remained unchanged with increasing crosslinker content. With the ratio decreasing from 15/1 to 9/1, G'' was increased slightly from 32.81 to 46.25 Pa, as the ratio continued to decrease from 9/1

Fig. 4 Elastic Moduli (G') and Viscous Moduli (G'') of Composite Hydrogel vs. Ratio of Polymer to Crosslinker

to 8/1, G' was decreased to 41.73 Pa inversely. Compared with slightly fluctuation of G'' , G' experienced a steady increase from 309.85 to 522.05 Pa. It can be denoted by the increasing crosslinking points among polymer chains because of increasing chromium acetate content, accordingly, the crosslinking density per structure unit was increased. The higher the crosslinking density, the more densely the three-dimension network structure of composite hydrogel. When applied constant stress of 50 Pa, composite hydrogel stored much energy by elastic deformation, causing the increase of elastic moduli (G'), that is why composite hydrogel showed a distinct rigidity of viscoelastic solid, while the weak fluidity led to the decrease of viscous moduli. Additionally, as the performance of viscoelastic solid highlighted, the distinct elasticity caused large elastic deformation to store much energy, resulting in a low proportion of energy dissipated by viscous moduli (G''), moreover, the large deformation caused the weak adhesion between hydrogel and measuring geometry¹⁷⁾, which also led to the decrease of viscous moduli.

Compression strength of nanocomposite hydrogel was present in Fig. 5. When the ratio of polymer to crosslinker decreased (crosslinker content increased) from 15/1 to 10/1, the compression strength showed initial increase from 62.9 to 120 kPa m⁻¹, as the ratio continued to decline, the compression strength experienced a peak value, then began to reduce to 75.18 kPa m⁻¹ as the ratio decreased to 8/1. During compression tests, compression strength was determined by both its mechanical strength and adhesion between hydrogel and wall of casing. On the one hand, within the crosslinker content threshold in which polymer chains involved orderly crosslinking reaction with crosslinker, the increasing crosslinker points induced the increasing crosslinking density of network structure, consequently, macro strength of composite hydrogel showed robust,

Fig. 5 Compression Strength of Composite Hydrogel vs. Ratio of Polymer to Crosslinker

indicating compression strength was proportional to the ratio. Beyond the threshold, excessive crosslinking caused disordered dispersion of crosslinking points, resulting in potential breaking points when the hydrogel was subjected to increasing applied stress, as a result, the compression strength was decreased. On the other, the compression strength was also dependent on the adhesion that is correlated to viscous moduli (G'')¹⁷⁾, as shown in Fig. 4, G'' became decreased with the ratio of polymer to crosslinker decreased to 9/1, besides, as a viscoelastic solid, the hydrogel was dominated by elasticity, which all weakened the adhesion between composite hydrogel and wall of casing. When the increasing nitrogen pressure was applied on hydrogel, the hydrogel was easily detached from the wall of casing due to its weak adhesion, which also resulted in prematurely broken through of hydrogel.

3.3. Enhancement of Nano Silica on Nanocomposite Hydrogel

Silica nanoparticles were added to enhance the strength of nanocomposite hydrogel. The silica content was varying from 0 to 7 % to investigate its enhancement on viscoelasticity, as shown in Fig. 6. Both G' and G'' increased with the increasing silica content. At low silica content (0-0.5 %), G' was increased little and remained around 50 Pa. At medium silica content (1-3 %), G' was increased an order of magnitude, to 102.6 Pa and 156.8 Pa, respectively. While at high silica content (5-7 %), G' was increased significantly to 502.2 Pa and 975.5 Pa, more than 15 and 30 times respectively larger than that of hydrogel without containing silica. By contrast, viscous moduli (G'') was only increased to 24.72 Pa from 5.865 Pa, as the silica content went up to 3 %. Even the silica content increased to 5 % and 7 %, G'' was increased to 34.37 Pa and 80.8 Pa, suggesting that when the silica content reached 7 %, the viscous moduli would be significantly increased. In addition, the silica contributed

Fig. 6 The Effect of Silica Content on (a) Elastic Moduli (G') and Viscous Moduli (G'')

more to G' than G'' , which may be attributed to the intrinsic properties of silica nanoparticles that was featured by small size, high specific surface and distinct rigidity. After adding into polymer crosslinking system, silica particles dispersed in the system and improved the ability to store and dissipate energy when the hydrogel occurred deformation under applied stress, which led to the increase of elastic moduli (G') and viscous moduli (G'').

As shown in **Fig. 7**, the compression strength was enhanced dramatically as the silica content increased. When the silica content increased to 1 %, the compression strength was enhanced from 70.8 to 85.84 kPa m^{-1} , with silica concentration continually increasing to 5 %, the compression strength was increased to 121 kPa m^{-1} , 1.7 times higher than that of hydrogel without silica. After the silica concentration reached 7 %, the compression strength had sharply increased to 142 kPa m^{-1} , indicating that solid silica particles can significantly enhance the macro compression strength of composite hydrogel. During the compression strength tests, the

Fig. 7 Compression Strength of Composite Hydrogel with Increasing Silica Concentration

Fig. 8 Composite Hydrogel Bubbled under Nitrogen Pressure

nitrogen continued to enter the bottom of hydrogel through the pipeline, leading to the increasing pressure applied on the hydrogel. When the mechanical strength of hydrogel was strong enough and formed tight adhesion with the wall of casing, the hydrogel could resist the increasing pressure by occurring elastic deformation to dissipate energy. Therefore, with the improvement of viscoelasticity present in **Fig. 6**, the compression strength increased undoubtedly. Whereas the nitrogen pressure increased to a critical value, which the hydrogel failed to withstand, then with the center that the strength was weakest bubbled from inside, as shown in **Fig. 8**, the hydrogel was broken through instantly.

The addition of nmSiO₂ can enhance the mechanical strength of hydrogel for killing application, and the pumpability of composite fluid needs to be studied because it has to be pumped into downhole during kill-

Fig. 9 Thixotropic Property of Composite Fluids with Varying Silica Content

(a) Nano-silica (magnified 50,000 times); (b) Polymer hydrogel without silica; (c) Polymer/silica nanocomposite hydrogel.

Fig. 10 ESEM Images of nmSiO₂ and Hydrogel

ing well. The thixotropic property of composite fluids with varying silica content ranging from 0 to 7 % is shown in **Fig. 9**. The composite fluids were all shear-thinning type, which means the apparent viscosity decreases as the fluids are sheared by stirring or shaking. This performance promises the excellent pumpability during killing operation.

Figure 10 present ESEM images of silica nanoparticles, hydrogel without silica and composite hydrogel with silica content of 3 %. The results showed that silica particles present spherical morphology with the size ranging from 50 to 60 nm, and aggregated easily because of nanometer size and high specific surface.

Figures 10(b) and **10(c)** compared the microstructure of hydrogel without silica and nanocomposite hydrogel that were both magnified 1000 times. It can be seen that the hydrogel without silica showed irregular three-dimension network and sparse network framework, with the pore size of network ranging from 50 to 100 μm. Whereas for nanocomposite hydrogel, regular network structure was clear with the pore size 10-25 μm. Silica nanoparticles adsorbed onto the coarse main-branch and thin branches of three-dimension network in aggregation, besides, filled into the entangled pores. Although the aggregates dispersed on the polymer chains was larger than that filling in network, suggesting silica particles were inclined to attach on network chains compared with filling in the network. Therefore, silica nanoparticles enhanced the hydrogel strength in the form of adsorbing onto the network skeleton and filling in the network pores. Moreover, within two-dimension layer structure, adsorption from silica narrowed the space between adjacent network chains, and also decreased the flowing of free water thus increased the flow resistance, which made the entanglement of crosslinking chains strengthened. Meanwhile, within three-dimension network, the space between vertical layers of network was compressed, leading the moving friction between layers increasing. Apparently, the distribution of silica strengthened the micro network structure of hydrogel and thus enhanced the macro strength of hydrogel. Therefore, under the shear stress, hydrogel not only occurred elastic deformation to accumulate energy, but accelerated the dissipation of excess energy by the dispersion of silica particles to prevent against fracture.

4. Conclusion

In conclusion, the static strength, viscoelasticity and compression strength of composite hydrogel were influenced by polymer content, the ratio of polymer to chromium acetate crosslinker. Elastic moduli (G'), viscous moduli (G'') and compression strength all increased with the increasing polymer and silica content. G' was proportional to the ratio of polymer to crosslinker, however, G'' kept stable with the decreasing ratio. Compression strength experienced an initial increase then decrease with the decreasing ratio of polymer to crosslinker. Moreover, the enhanced mechanism of nmSiO₂ on composite hydrogel performance was investigated. Silica nanoparticles adsorbed onto the network chains and filled into the network pores to incorporate the advantages of silica to the crosslinking hydrogel system, therefore to enhance the mechanical strength of hydrogel for better application in well killing. The study on high strength polymer/silica composite hydrogel promoted the future application of nanocomposite materials on oilfield well killing.

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